Metal Oxide Nano-Array Catalysts for Low Temperature Diesel Oxidation

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& Institute of Materials Science
University of Connecticut, Storrs, USA

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Washington D.C.

Project ID #: ACS095

Project Overview

Overall objective:

Develop a unique class of cost-effective and high performance metal oxide based nano-array catalysts for low temperature CO and HC oxidation, 90% conversion at 150 °C or lower

Timeline

- Project start date: 10/01/2014
- Project end date: 12/31/2017
- Percent complete: ~80%

Budget

- Total project funding
  - DOE share: $1,450,000
  - Contractor share: $380,139

Barriers

- Barriers addressed
  - From DOE Vehicle Technologies Multi-Year Program Plan
    - 2.3.1.B: Lack of cost-effective emission control
    - 2.3.1.D: Durability
  - Responsive to USDRIVE ACEC Tech Team Roadmap, Low Temperature Aftertreatment Workshop Report

Team Partners

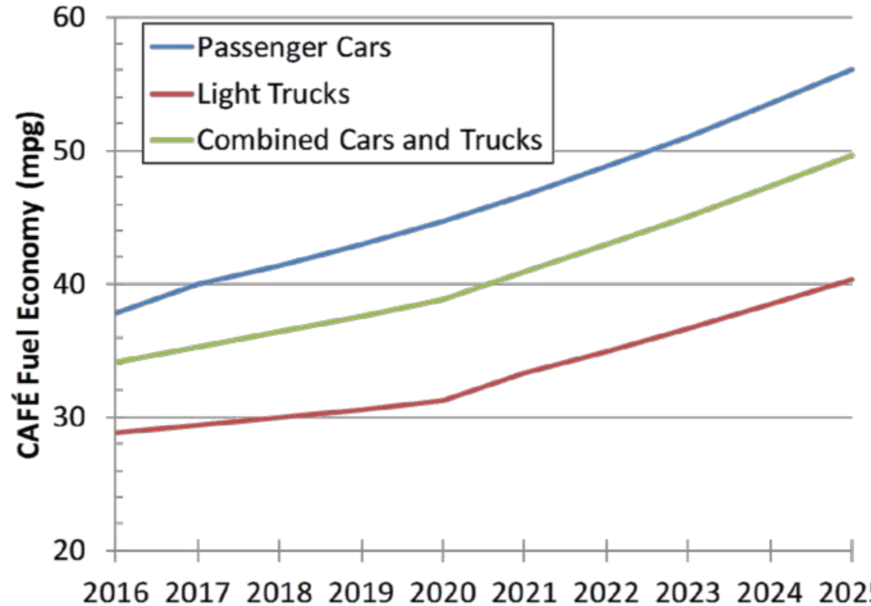
- ORNL, Umicore, and 3D Array Technology LLC

Project Relevance

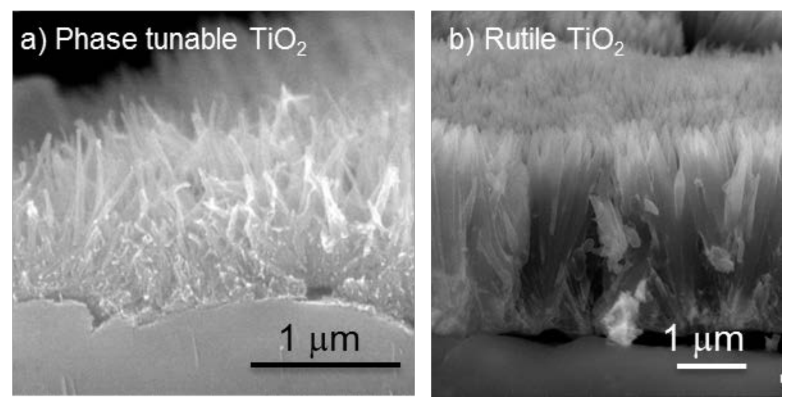
- Improved fuel economy standards will require advanced combustion engines with greater fuel efficiency and consequently **low exhaust temperatures**
- Challenges:
  - Stricter emissions standards
  - Greater HC + CO emissions
  - Low reactivity at 150°C

→ **New technology needed**

→ Investigate nano-array catalysts for low-cost pathway to 90% conversion of HC + CO at 150°C

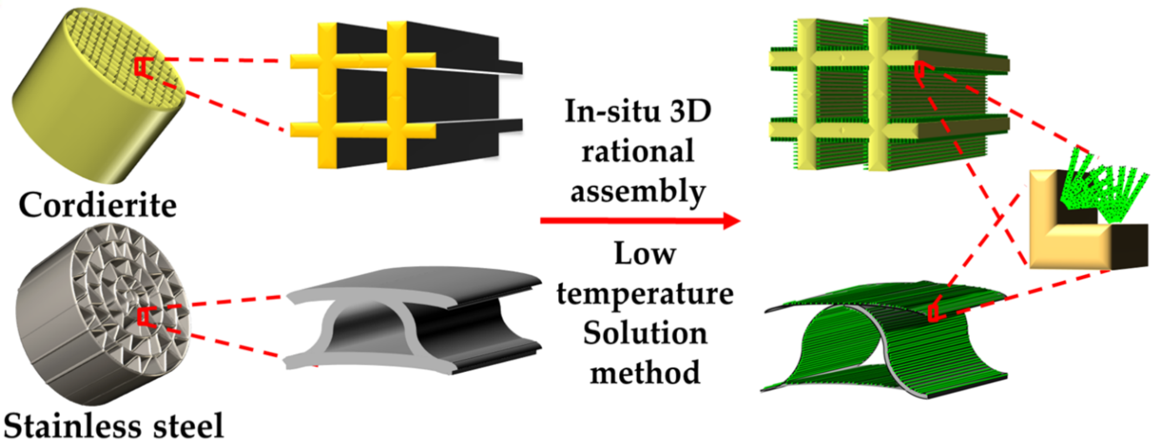


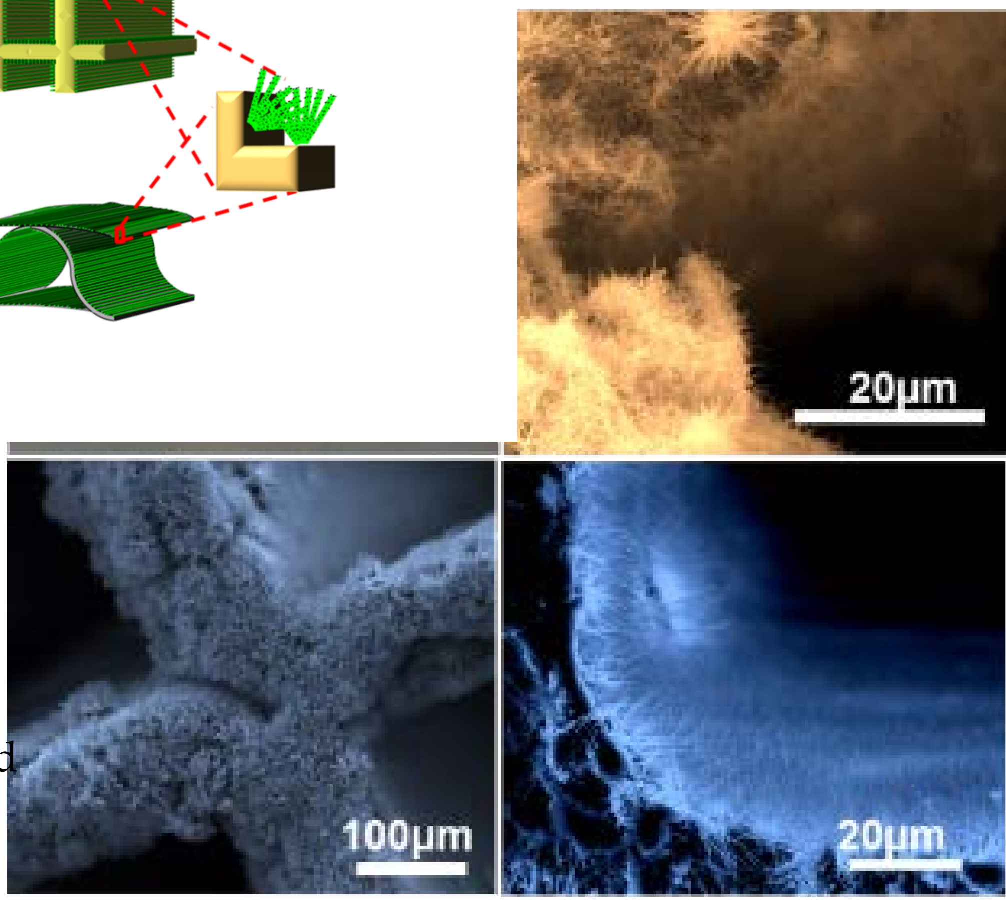
C. DiMaggio, "ACEC Low Temperature Aftertreatment Program", 6/21/12.



Low-temperature processed and hydrothermally stable TiO_2/Pt based nano-array catalysts: a) phase tunable TiO_2; b) mesoporous rutile TiO_2.

In-situ Growth of Nano-arrays onto Honeycomb Monoliths

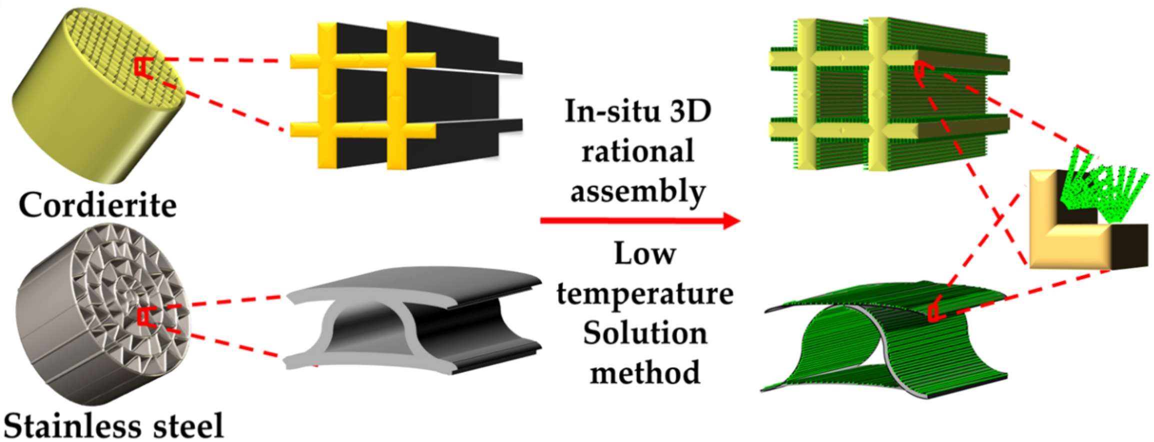


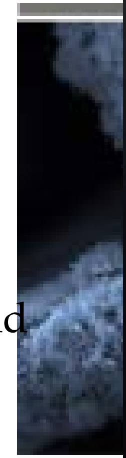


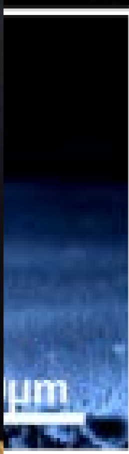
- In-situ solution-based growth of (nanostructure array) nano-array on monolith
- Free of binders, robustness due to strong substrate-array adhesion
- Reduced PGM and other materials
- Improved efficiency due to size, shape, and structure
- Hydrothermally stable (e.g., TiO_2, CeO_2, Al_2O_3)

Ren, Gao et al., *Angew. Chem. Int. Ed.*, **2014** , 53(28), 7223–7227. Guo, Ren, Gao et al., *Nano Energy*, **2013,** 2, 873-881.
Ren, Gao et al., *J. Mater. Chem. A.*, **2013** , 1, 9897-9906 .

In-situ Growth of Nano-arrays onto Honeycomb Monoliths







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- Reduced PGM and other materials
- Improved efficiency due to size, shape, and structure
- Hydrothermally stable (e.g., TiO_2, CeO_2, Al_2O_3)
- **Demonstrated on a range of scales**

Ren, Gao et al., *Angew. Chem. Int. Ed.*, **2014** , 53(28), 7223–7227. Guo, Ren, Gao et al., *Nano Energy*, **2013,** 2, 873-881.
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Responses to AMR comments
(Project period: 4/1/2016-03/31/2017)

- **Approach** very unique is the growth of nano-array catalysts in an existing honeycomb support... In order to downselect appropriate materials to advance to the next level, **realistic test conditions and aging treatments must be employed sooner**. …the in-situ growth of nano-array catalysts on monoliths is very interesting, although the reviewer wondered how relevant this would be commercially. … **how possible is the scale-up of this coating method, how durable are the nano-arrays, and are they more susceptible to thermal stresses, sintering, and aging.** .... The reviewer pointed out **the need to have assessed S poisoning effects** by now (based on comments from last year). ....

Responses to AMR comments

(Project period: 4/1/2016-03/31/2017)

- **Approach** very uniq
materials to advance
of nano-array catalys
how possible is the
stresses, sintering, a
comments from last

Responsive Actions
Focus on testing under realistic simulated gases and mixture gases for species inhibition/promotion understanding
Focus on evaluation of mechanical/hydrothermal stability following protocoled procedures
Aging studies being performed (including sulfur exposure); *Array design over PGM doping and CeO_2 or Al_2O_3 decoration for water/S mitigation;* *Surface area tracked for catalysts*

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- **<u>Technical Accomplishments:</u>** minor progress had been achieved in the characterization of multiple catalyst formulations using more realistic feed conditions and aging treatments... However, **poisoning effects were not addressed and comparison to a reference, traditional PGM catalyst was not done as a benchmark**. The reviewer noted that **from a manufacturing perspective, using a growth technique to deposit an active catalyst material on a substrate may preclude the adoption of this technology. The reviewer inquired as to whether any progress has been made to reduce this challenge** …Interesting results have been obtained, ….**more work needs to have been done using the ACEC protocol compositions with HTA**, which they have begun… One concern is that the Pt size increased due to HTA, which again brings up the question as to **the nano-array stability**. **Current testing methods do not allow for separation of kinetic and mass transport properties** … The reviewer noted that transition metal results on Slide 12 are of limited value because they **were collected under totally unrealistic conditions.** ….

- **<u>Future plans:</u>** The reviewer noted that lots of work remains and it may be necessary **to focus on the most promising one or maybe two of the catalyst systems** to get as complete a set of analyses as possible. …. **Some effort should be spent on understanding the role of kinetics versus mass transport**. . ... The reviewer stated that the project team indicated last year that more progress would be made testing under realistic conditions and aging methods

Responses to AMR comments
(Project period: 4/1/2016-03/31/2017)

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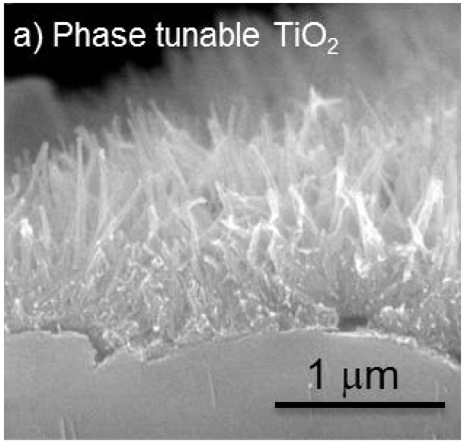
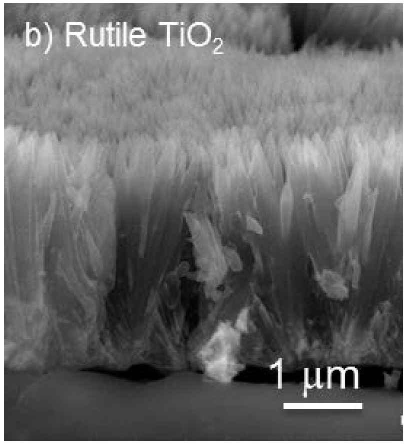
Focus on testing under realistic simulated gases and mixture gases for species inhibition/promotion understanding
Commercial DOC was employed as benchmark
Focus on scale-up synthesis; Full size substrates have been prepared for transient engine and engine test; Scalable low temperature TiO_2/Pt synthesis demonstrated
Kinetics of propane oxidation over Pt/TiO_2 have been studied

- **<u>Future plans:</u>** The re
two of the catalyst s
role of kinetics versus mass transport. . ... The reviewer stated that the project team indicated last year that more progress would be made testing under realistic conditions and aging methods

TiO_2 Nano-array Synthesis Technologies

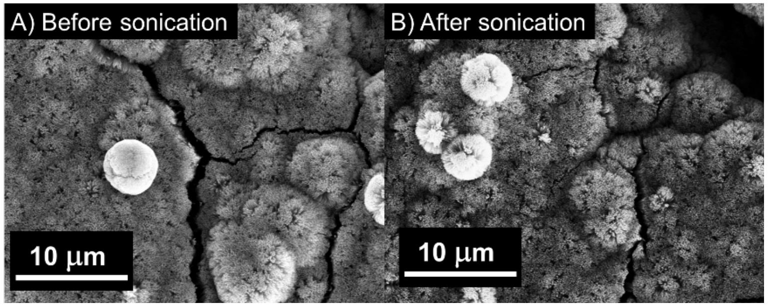
- Two synthesis/processing technologies to integrate TiO_2 nano-arrays onto ceramic monoliths: moderate (150 ^oC) and low (<= 90 ^oC) temperatures.





- Full size substrates (Φ5.66” x 3”) have been prepared for heavy-duty engine test. Transient engine test performed on samples (Φ2.5” x 3”)

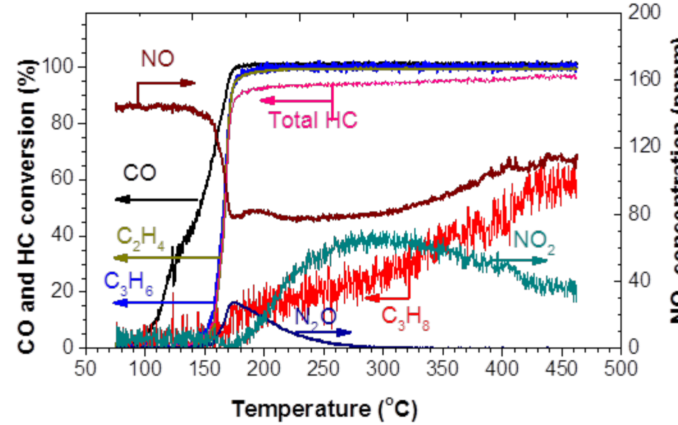
- In-situ growth results in excellent mechanical stability: negligible weight lost and morphology change after ultra-sonication test

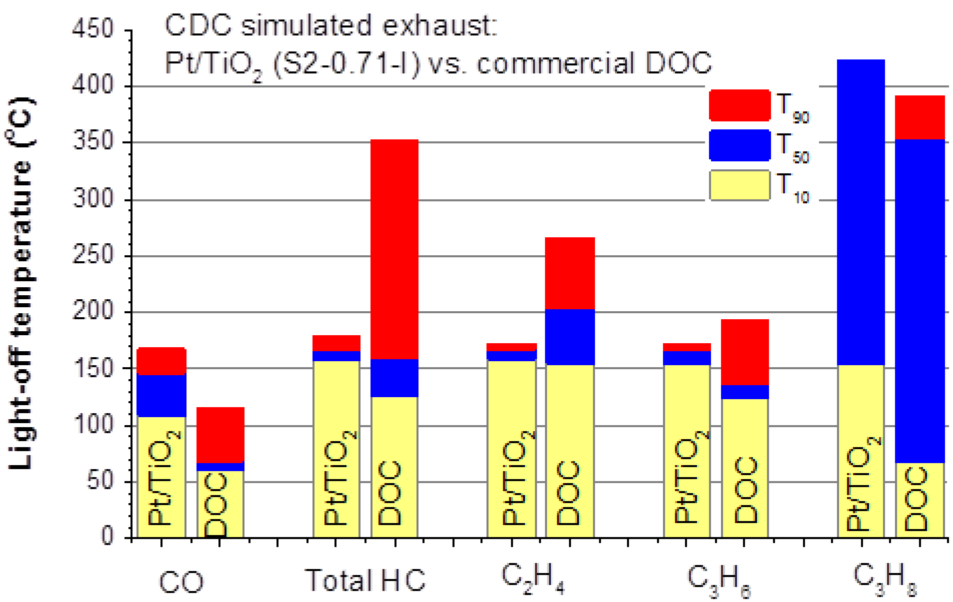


Pt/rutile TiO_2 Nano-array based Catalyst in CDC simulated exhaust

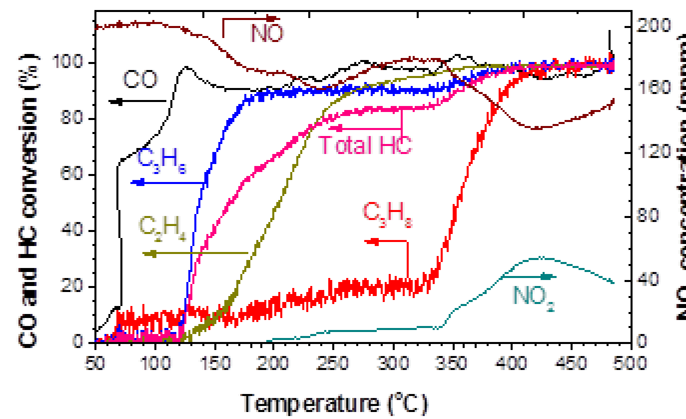
- Excellent performance of Pt/TiO_2 nano-array especially for unsaturated HC oxidation.
- T_{90} for THC as low as 178 °C vs. 355 °C for DOC
- Propane oxidation remains challenging → more on kinetics investigation later

Pt/rutile TiO_2 (20Pt g/ft^3)



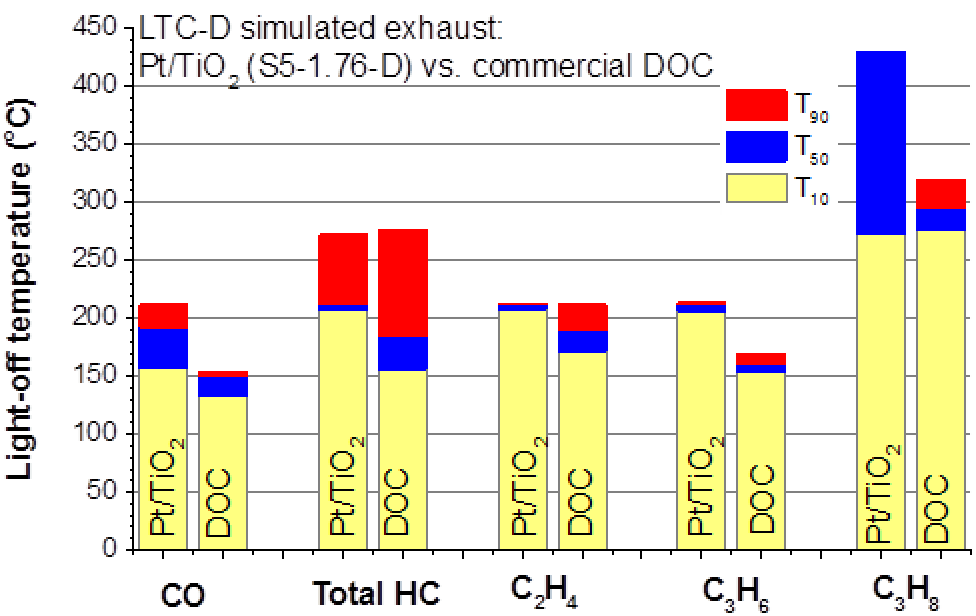


DOC bench-mark (25Pt/105Pd g/ft^3)

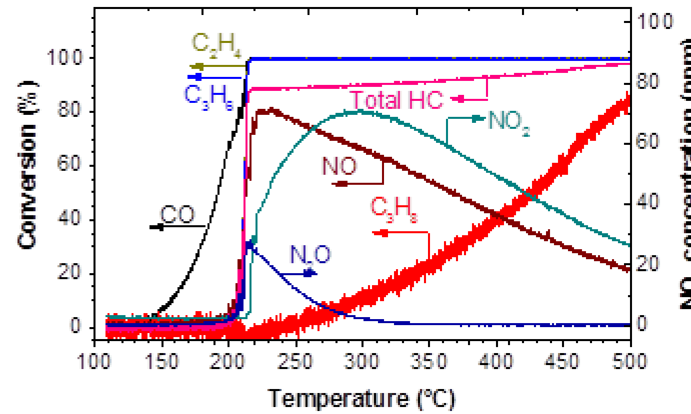


Pt/rutile TiO_2 Nano-array based Catalyst in LTC-D simulated exhaust

- Deactivated in LTC-D exhaust due to high concentration of CO and THC
- Comparable or even better for THC oxidation with DOC, despite 2.5 times lest PGM loading
- Out-performing for NO oxidation



Pt/rutile TiO_2 (50Pt g/ft^3)



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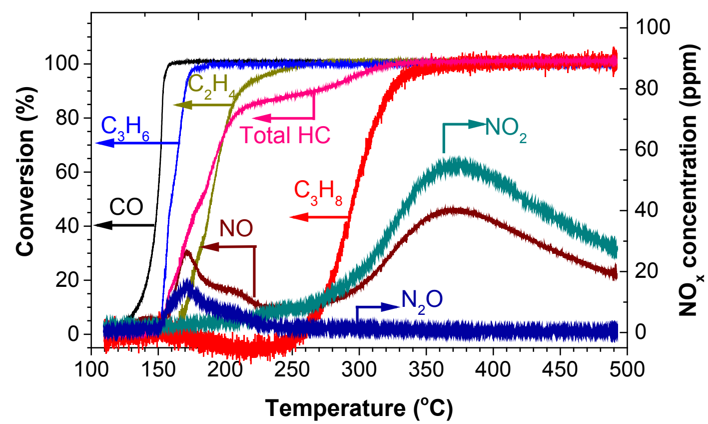
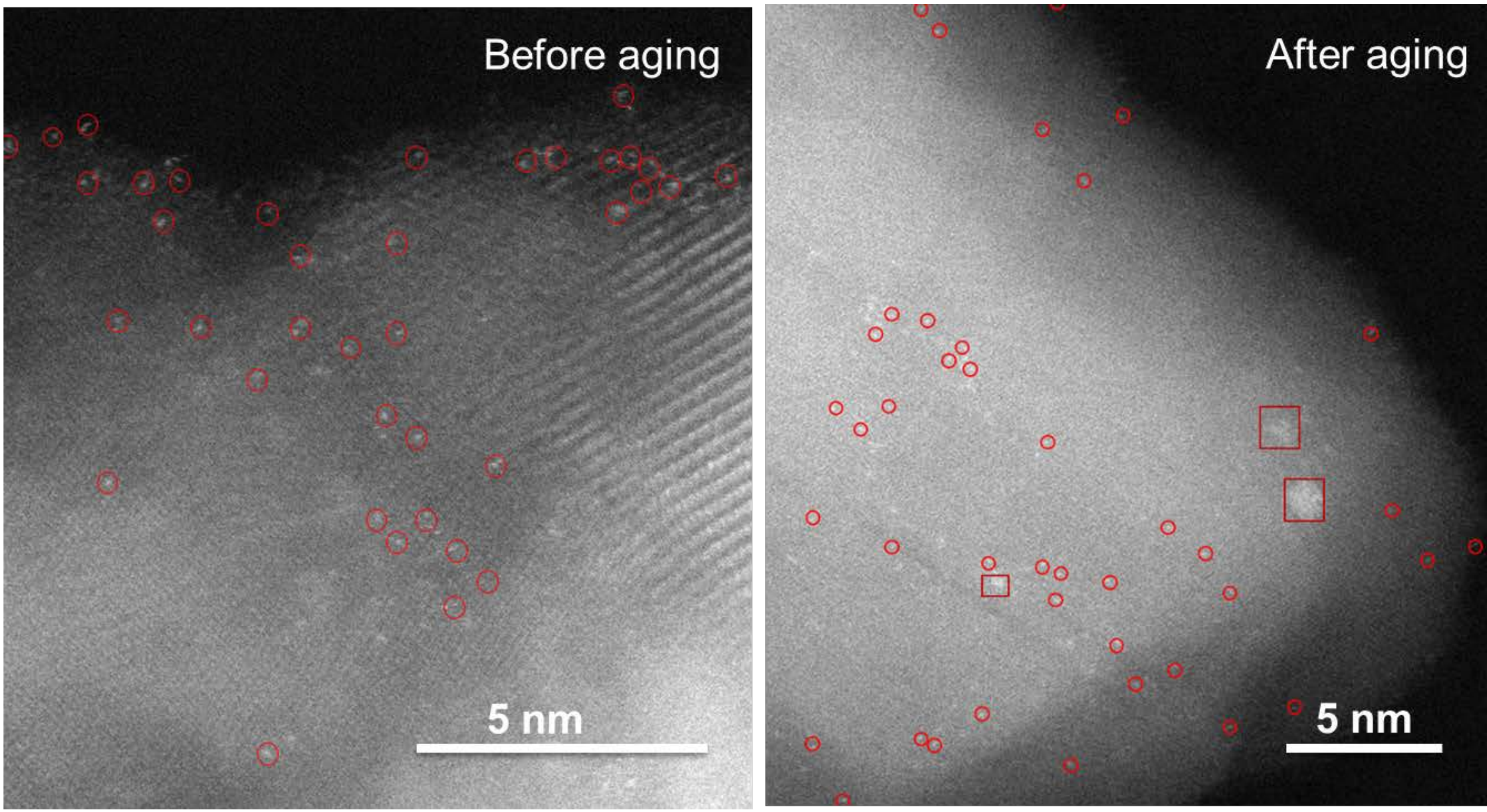


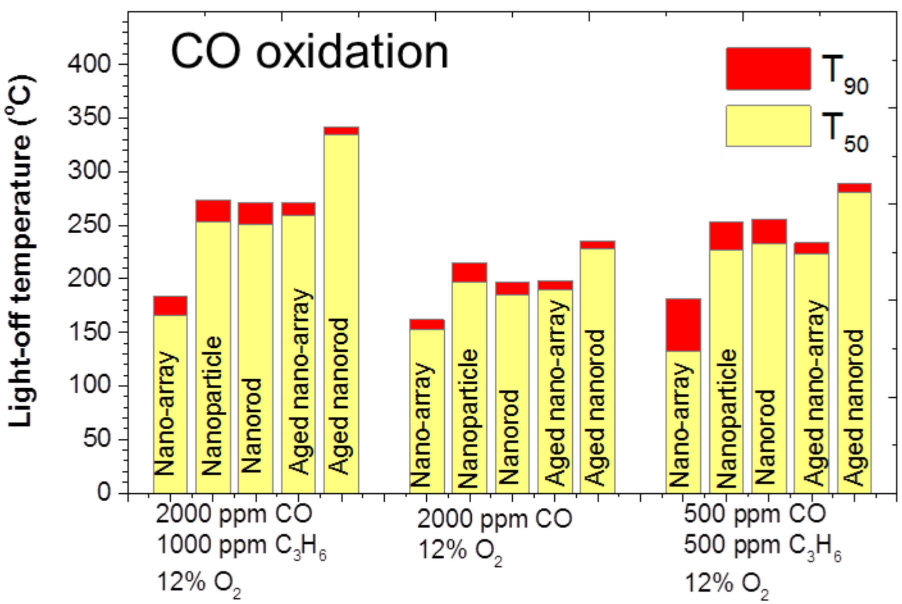
Pt/rutile TiO_2 Nano-array based Catalyst

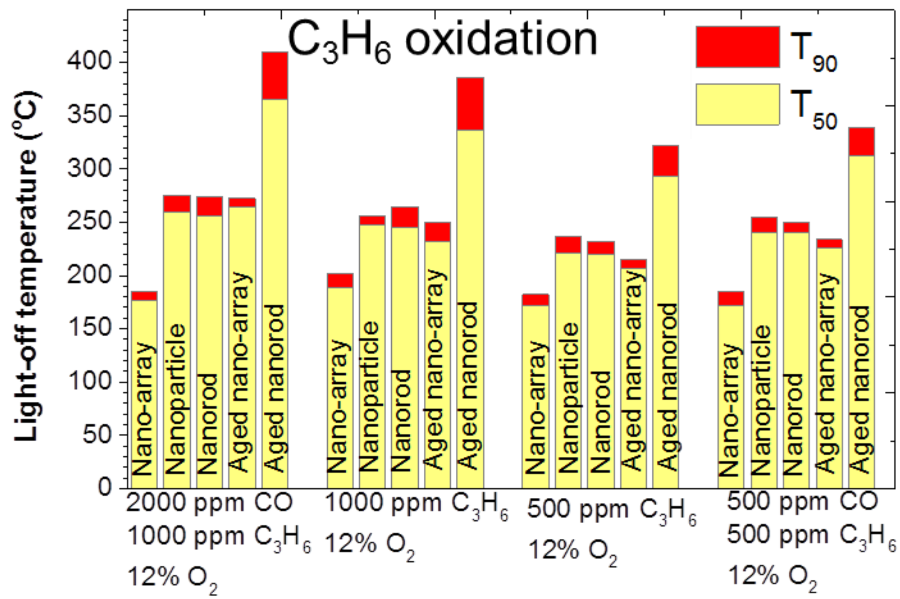
- Unique feature: Pt was dispersed as single atoms and sub-nanometer clusters
- Pt single atoms are stable even after hydrothermal aging at 700 ^{o}C for 4 hours



Hydrothermal stability study of Pt/rutile TiO_2 Nano-array

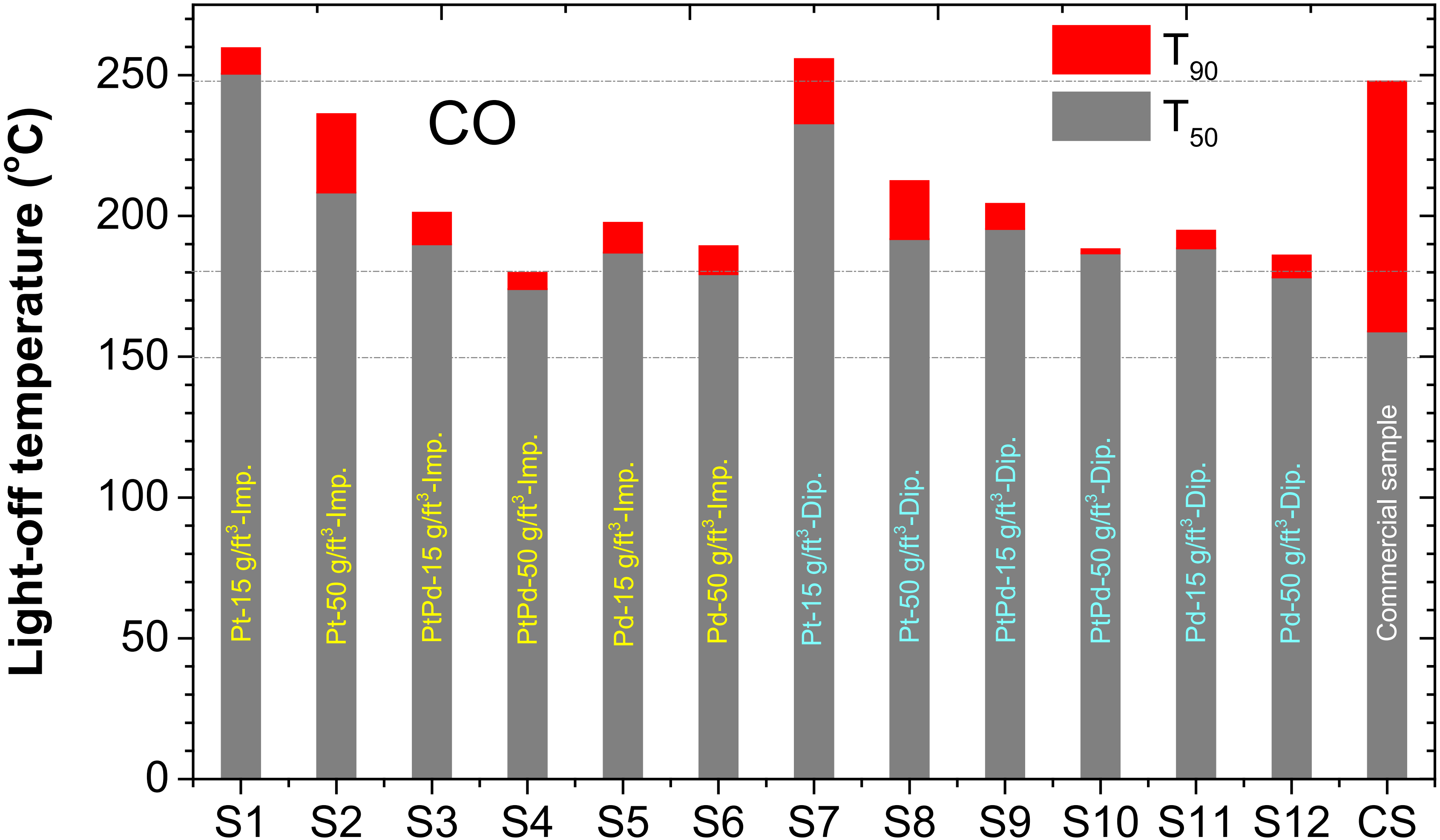
- CO and C_3H_6 as probe molecules
- Nano-array vs. Powder wash-coated samples: 20 g Pt/ft^3, ~12.5% TiO_2
  - Pt/TiO_2 nano-array showed better performance, less inhibition effects
- Effect of hydrothermal aging (700 ^oC for 100 hours):
  - deactivation, but performance is still on par with fresh wash-coating samples.
  - nano-array structure remains but surface area decreased from 45 to 16 m^2/g





Pt-Pd/rutile TiO_2 Nano-arrays for LTC-D

- Various Pt-Pd formulations (PGM loading, 3Pt/2Pd wt. ratio) tested
- Pt-Pd alloys showed better CO and HC oxidation



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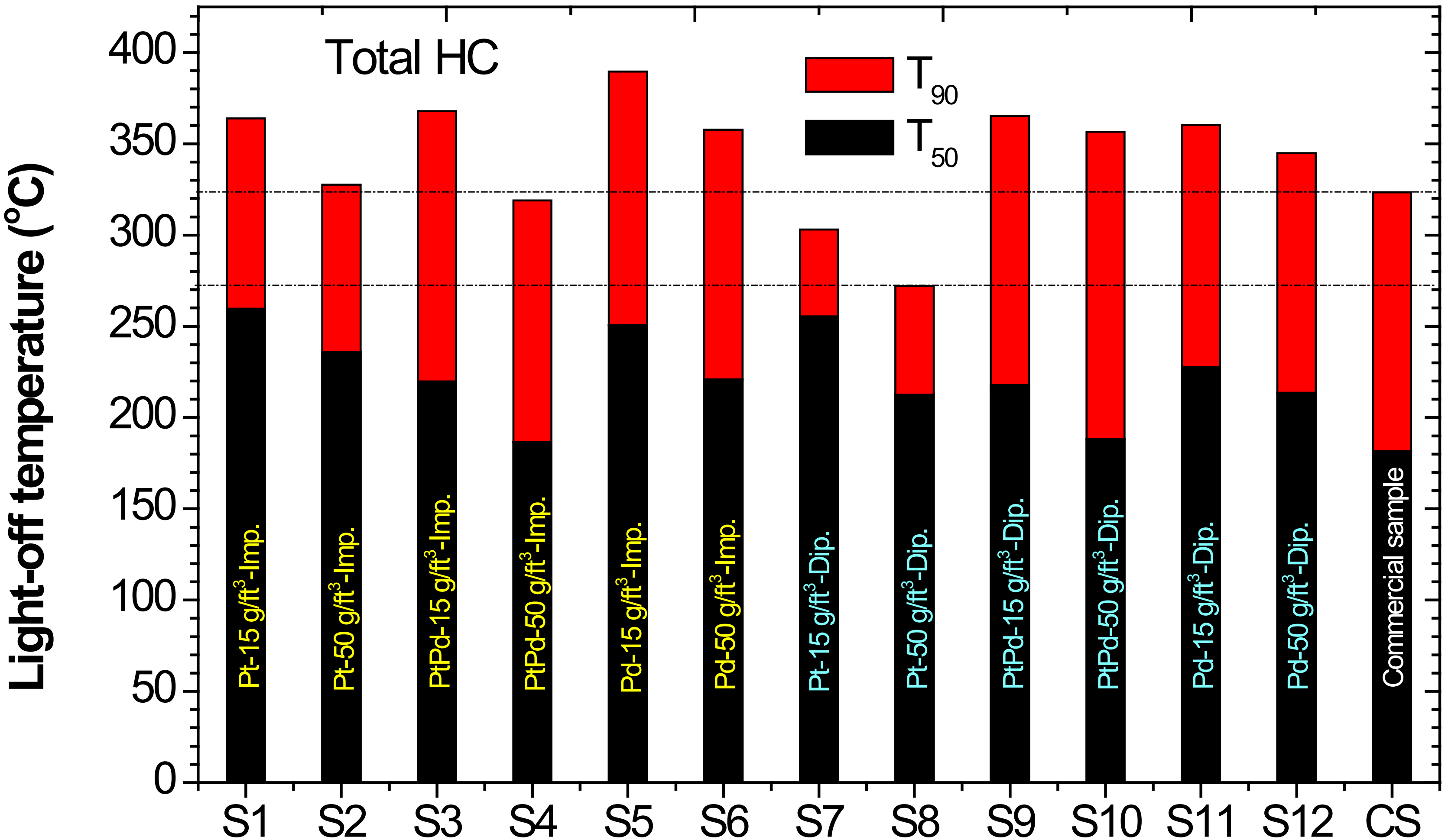
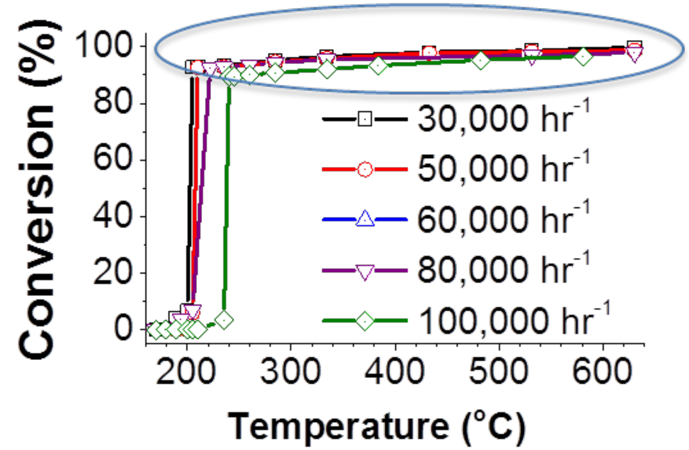
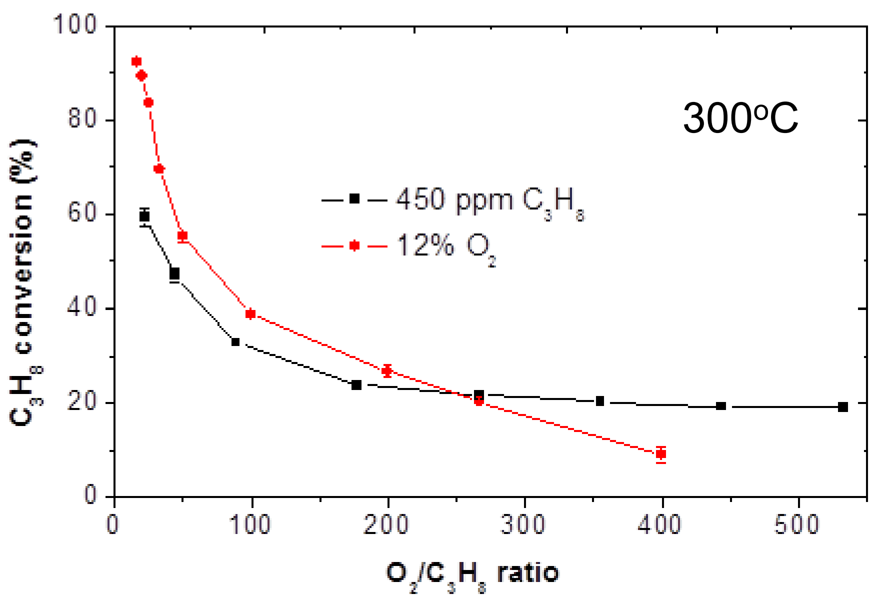


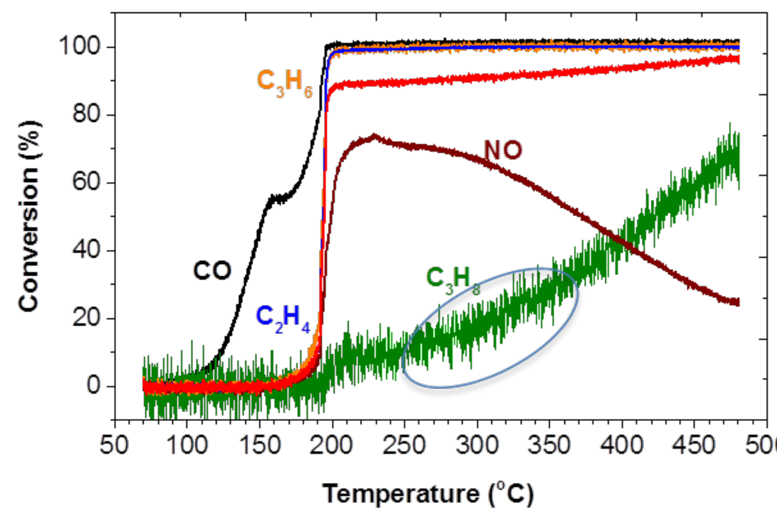
Kinetics study of Propane oxidation over ALD Pt/rutile TiO_2 Nano-array

- Excellent in high propane (0.8%) but poor in the CDC condition (55.4 ppm C_3H_8)
- Almost no dependence in space velocity up until 80,000 h^{-1} → excellent mass transport
- Plateau in high C_3H_8 conversion region
- Kinetics change due to varying O_2/propane ratio: competition for adsorption sites between C_3H_8 and O_2 & Pt oxidation states– unique for Pt catalysts → solution: Pt-Pd alloy catalysts



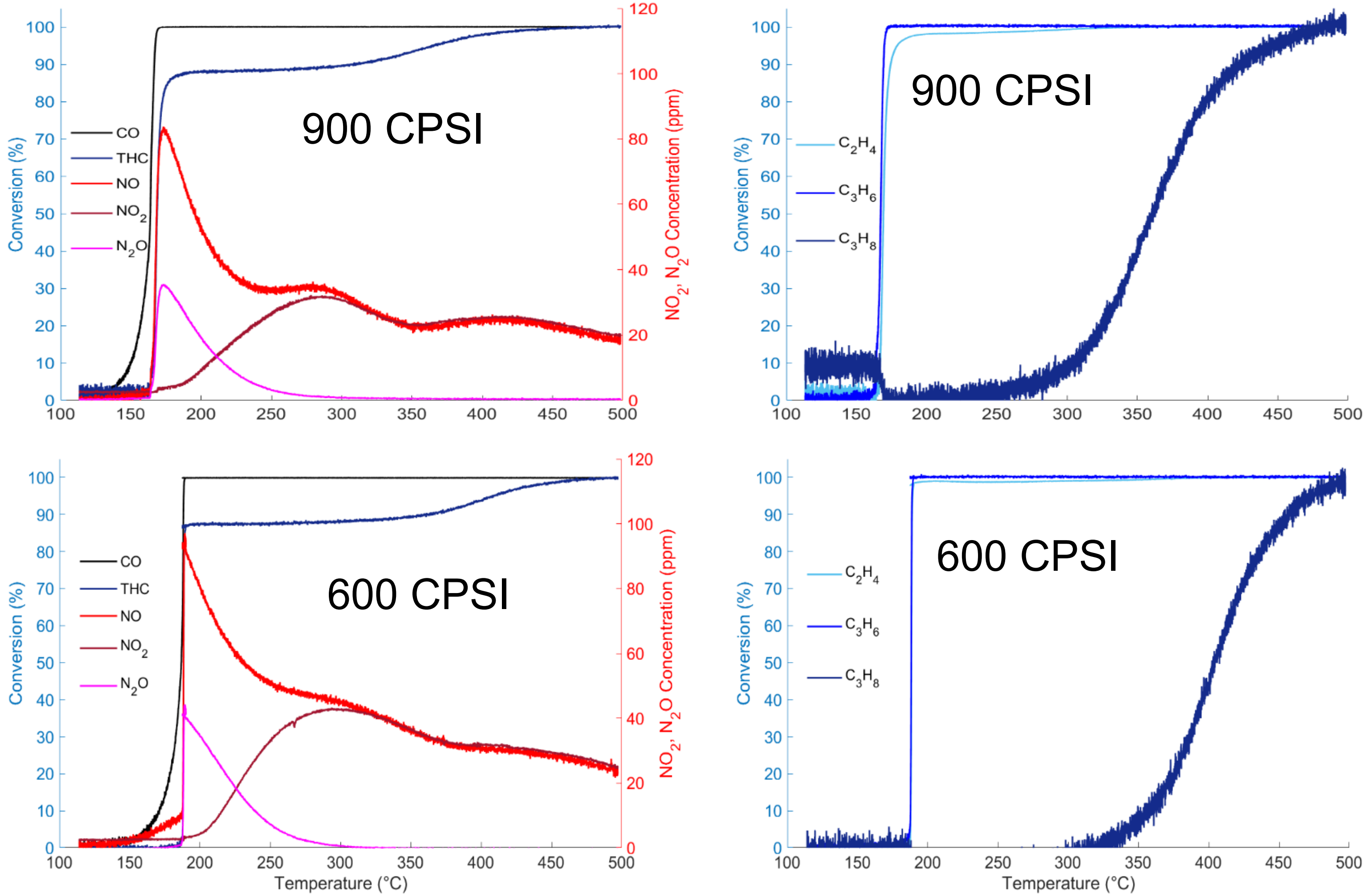
O_2/Propane ratio = 10



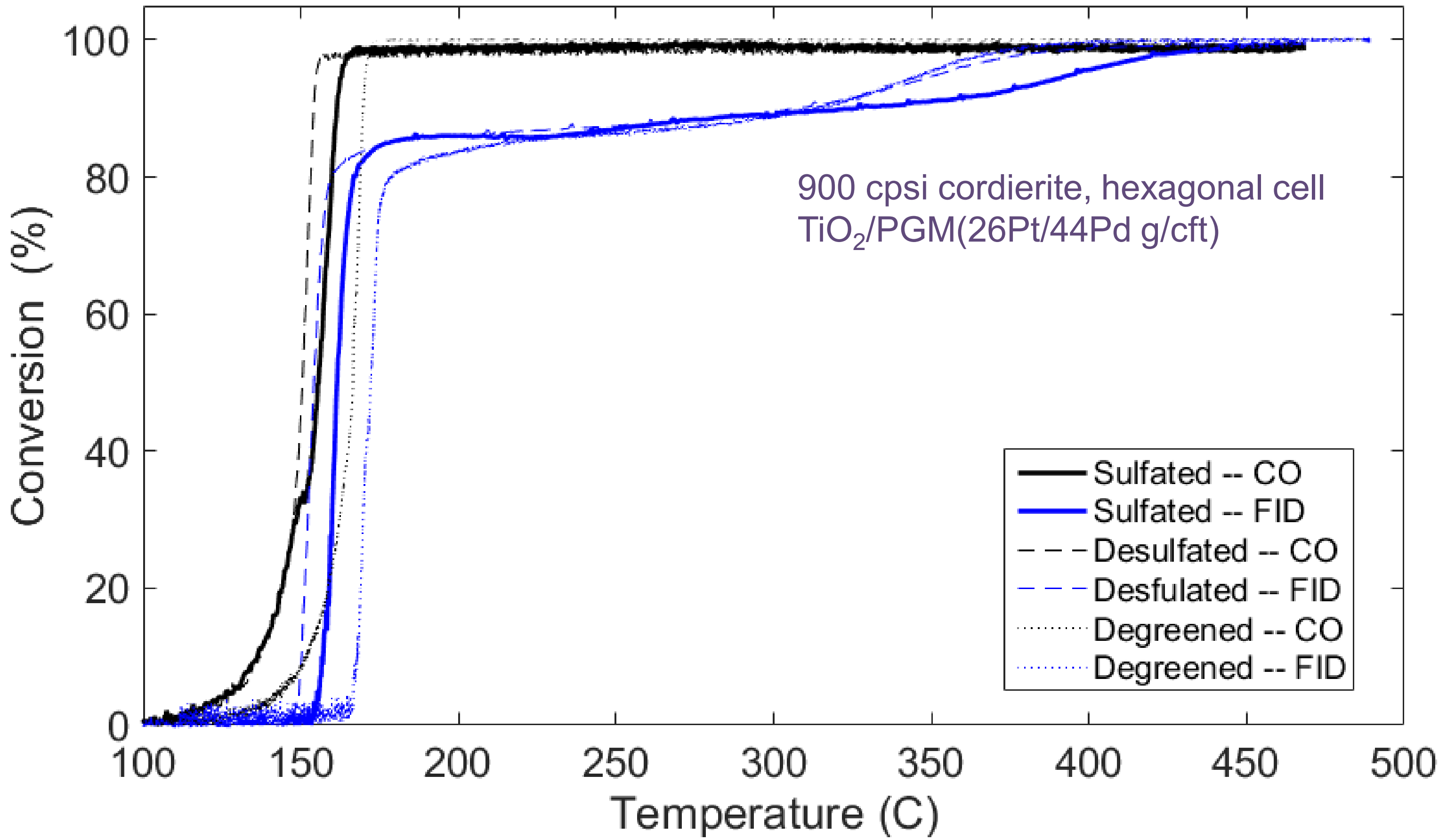


Pt-Pd/rutile TiO_2 Nano-arrays for LTC-D: Substrate effect

- In-situ growth addressed better back-pressure issue compared to wash-coating
- Higher cell density showed better performance due to higher catalyst loading and coverage under similar synthetic conditions (30Pt/20Pd g/cft)



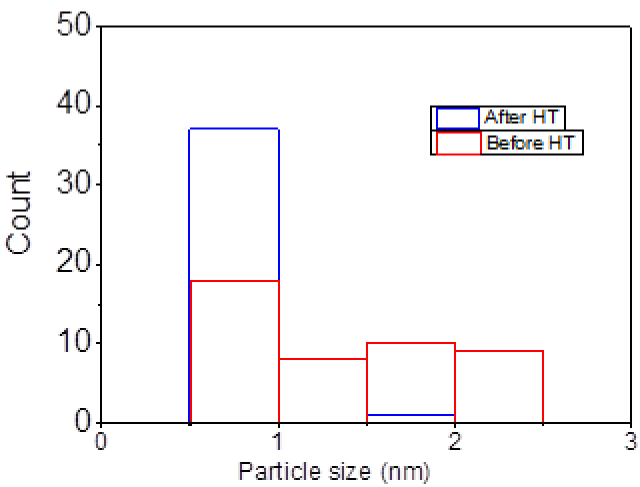
S-poisoning effect on Pt-Pd/rutile TiO_2 Nano-array Catalyst under LTC-D Mixture

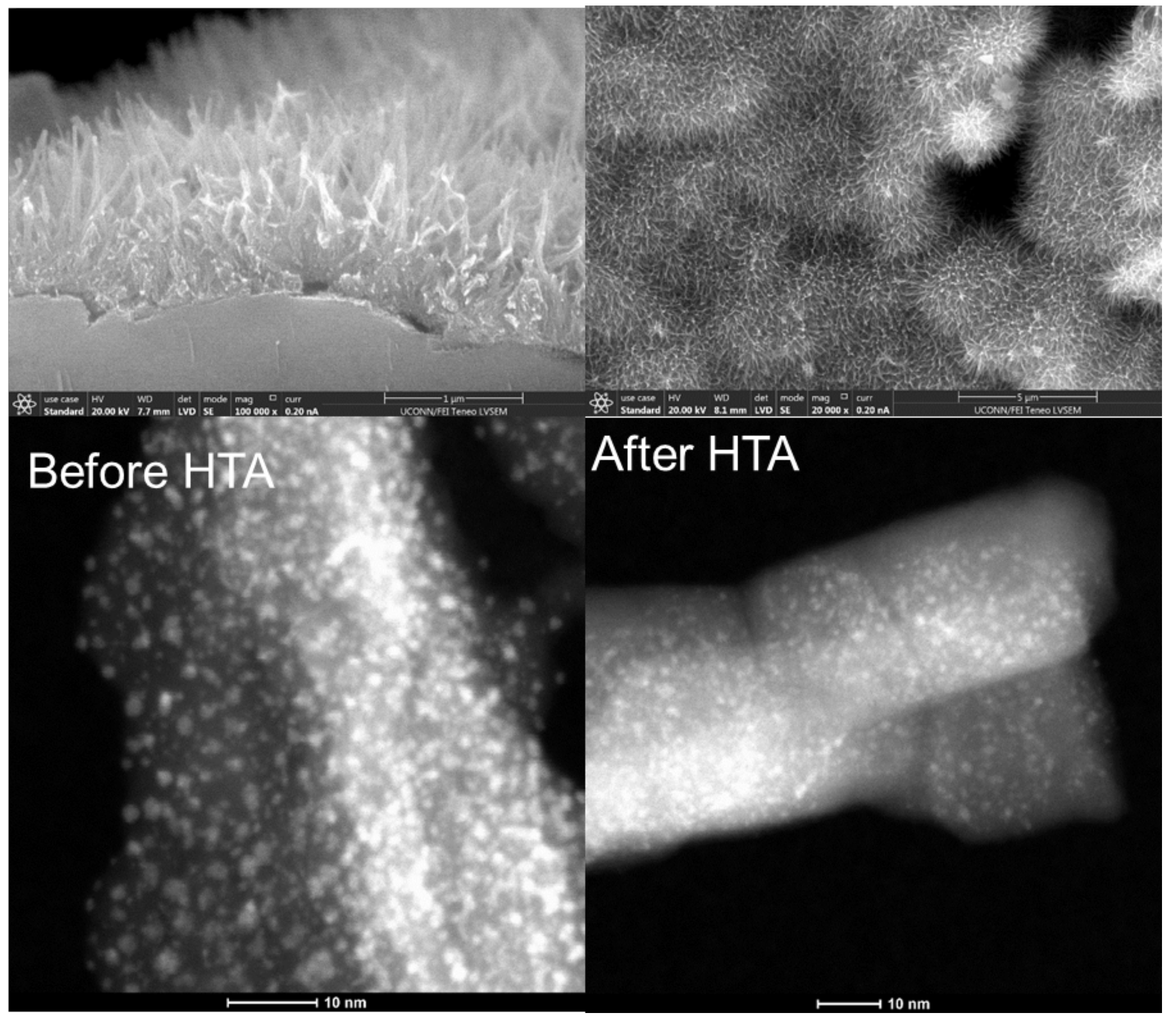


Step 1: 300°C, 5 ppm SO_2 added to the standard LTC-D mixture to sulfate the catalyst for 5 hours.
Step 2: Catalyst brought down to 100°C and ramped to 500°C for the sulfated light-off curve.
Step 3: Desulfation at 500°C by cycling 10% O_2 and 1% H_2 for 30 minutes (30 seconds per condition). 6% CO_2 and 6% H_2O in the common stream during this time.
Step 4: Catalyst down to 100°C and back up to 500°C under LTC-D conditions for desulfated light-off curve.

Pt/ TiO_2 Nano-array by Low-temperature Process

- Low processing temperature
- TiO_2 phase tunable by post-thermal treatment
- Pt particle seemed to be smaller after hydrothermal aging (700 ^oC, 100 h), likely with a Pt anchoring effect into TiO_2 relevant to SMSI effect

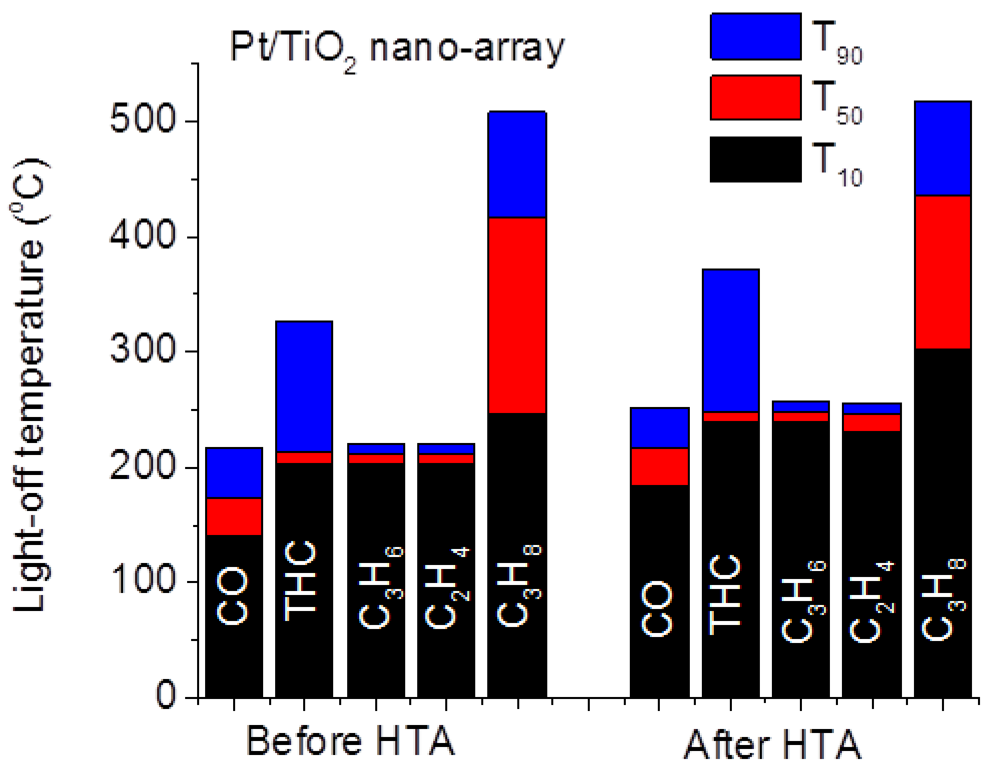




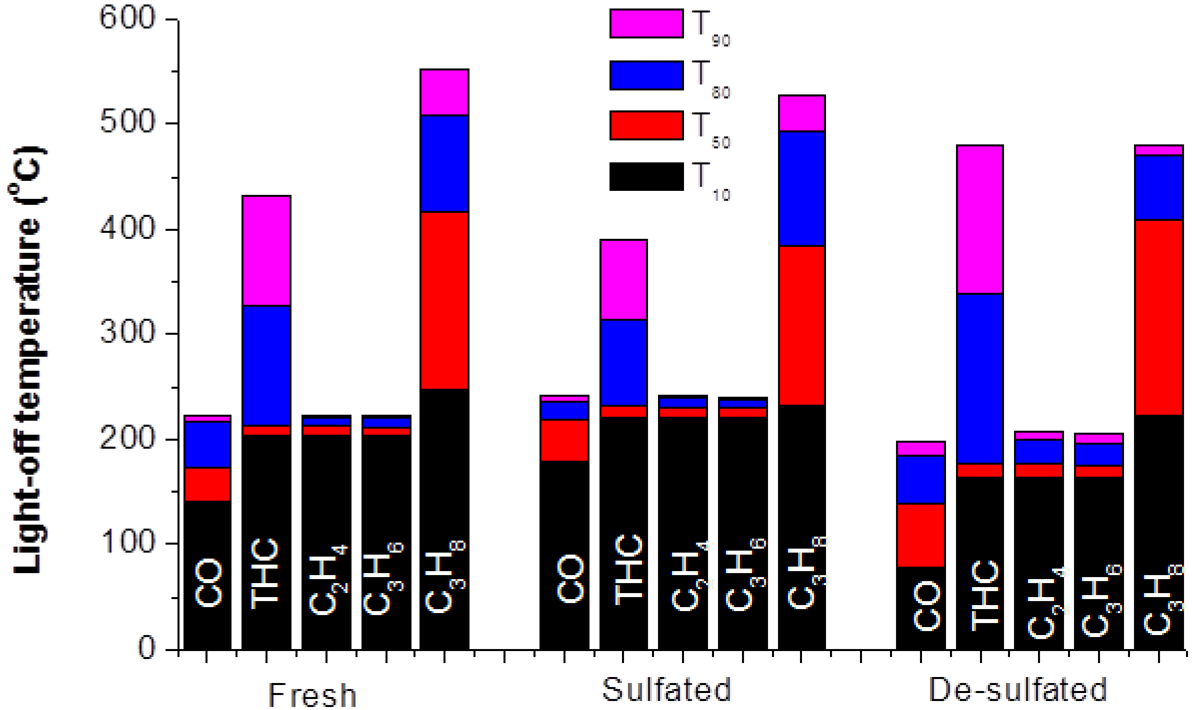
Pt/ TiO_2 Nano-array by Low-temperature Process for LTC-D: Hydrothermal stability

- Good performance with low Pt loading (50Pt g/ft^3)
- Excellent HT stability: after aging at 700 ^oC for 100 h, T90 increases by less than 40 ^oC

	T10	T50	T90
CO	70	106	180
THC	163	175	330
C_2H_4	163	175	196
C_3H_6	163	175	193
C_3H_8	220	410	470

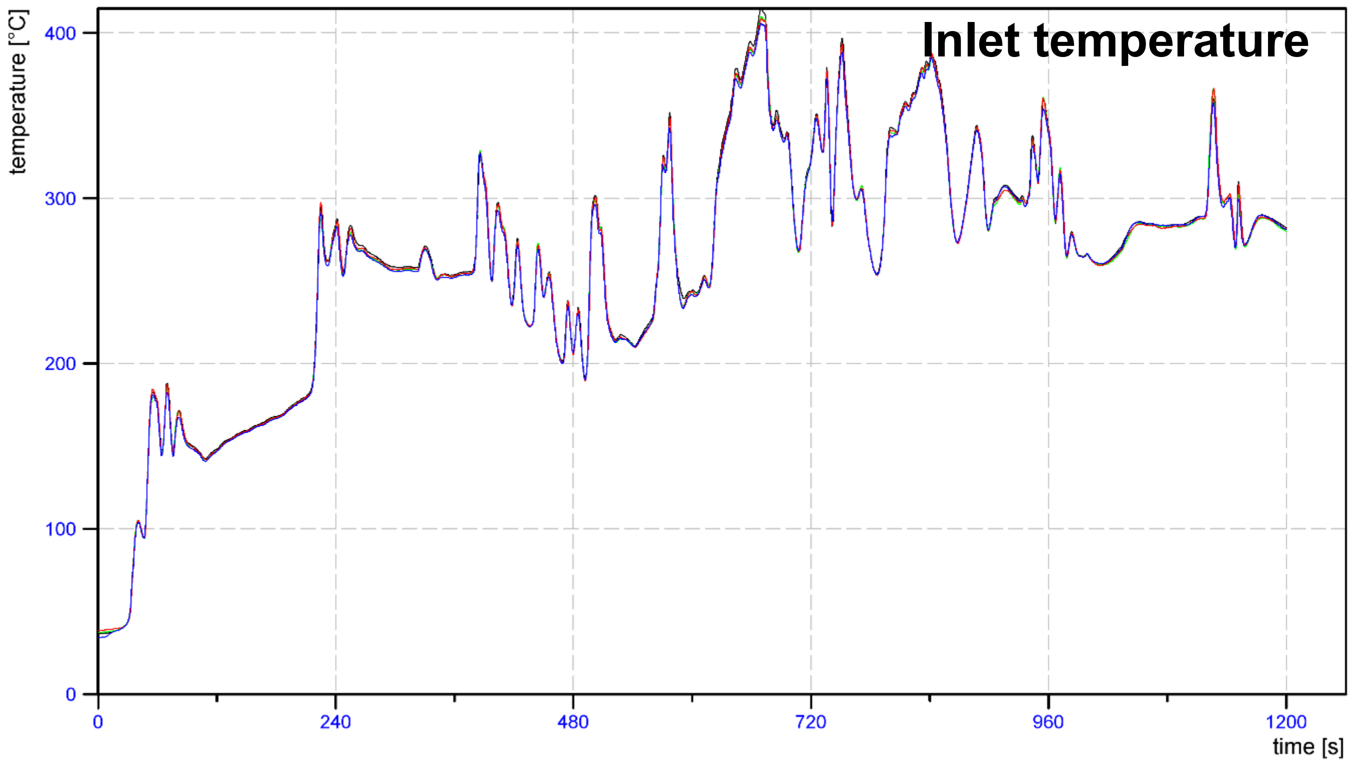


Pt/ TiO_2 Nano-array by Low-temperature Process: S poisoning Effects



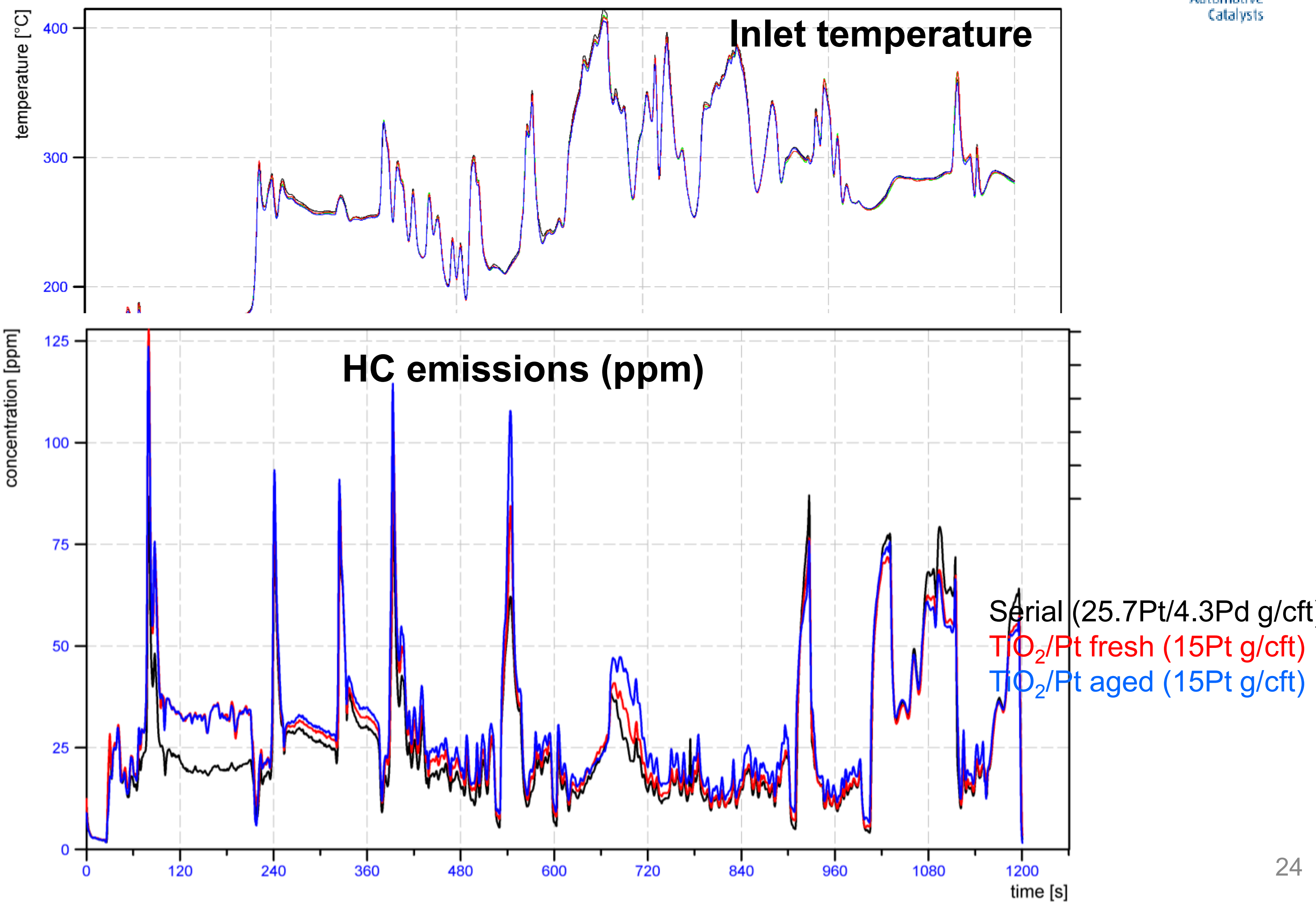
- Good S-poisoning resistance (50Pt g/cft):
  - CO and unsaturated HC: T90 increased less than 20 °C
  - propane oxidation is even better → lower T_{90} for THC after sulfation
- Recovered by H_2 treatment:
  - CO and unsaturated HC: T90 decreased ~ 50 °C, better than fresh sample

Pt/rutile TiO_2 Nano-arrays High dynamic test HC emissions



Serial (25.7Pt/4.3Pd g/cft)
TiO_2/Pt fresh (15Pt g/cft)
TiO_2/Pt aged (15Pt g/cft)

Pt/rutile TiO_2 Nano-arrays High dynamic test HC emissions



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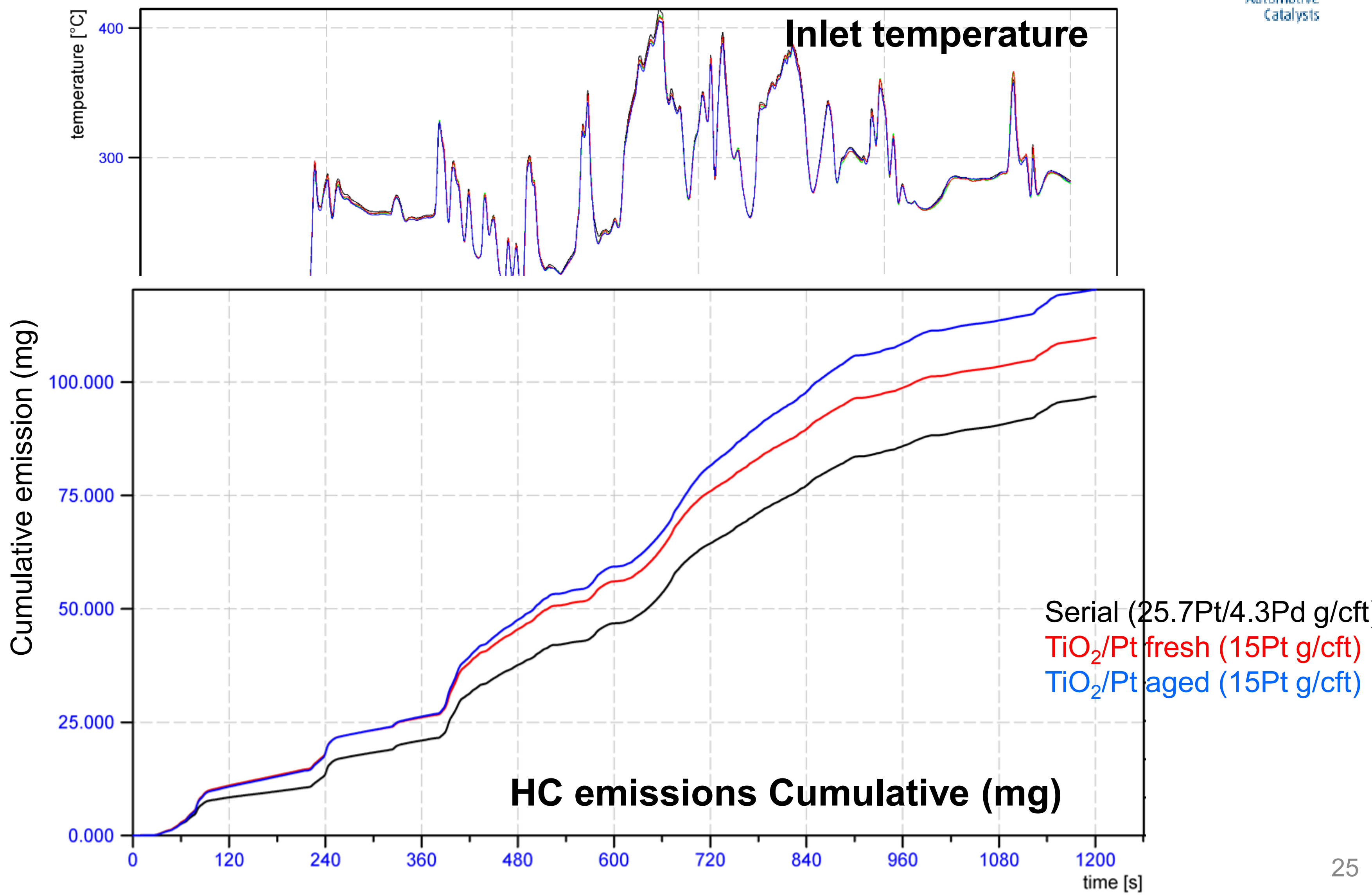

Engine Dynamometer Test

- 3 sets of TiO_2/Pt nano-array samples being tested at Umicore/FEV Inc., Auburn Hills, MI
- Specific Equipment:

  i. Engines:
     i. (MDD/HDD target) 2010 Cummins ISB6.7
     ii. (LDD target) 2014 Chrysler Eco diesel 3.0L

  ii. AC Dynamometer - 650HP max (Performance evaluation)

  iii. Hydrothermal oven aging capabilities

  v. HC injection and control

Conclusions and Future Work

1. **Approach:** in-situ growth of nano-array based catalysts onto various honeycomb substrates. Simulated exhaust gas and FTP transient cyclic conditions applied in catalytic oxidation testing.
2. **Relevance:** nano-array catalysts with low PGM and other materials usage, low temperature performance, and excellent robustness, meeting the needs of fuel economy, regulation, low temperature combustion, and environmental protection.
3. **Tech accomplishment:**

a) TiO_2/Pt based nano-array catalysts demonstrated excellent THC oxidation and CO oxidation performance under both CDC and LTC-D exhaust conditions. Under CDC condition, the THC 90% conversation temperatures approach 150^{o}C.
b) Hydrothermally aged TiO_2/Pt nano-array structures retained both structural and catalytic performance very well.
c) S-poisoned TiO_2/Pt nano-array structures retained both structural and catalytic performance with even better performance after desulfation.
d) FTP transient cyclic test showed that nano-array catalysts displayed similar conversion efficiency of THCs to that of reference benchmark;
e) Large scale nano-array devices engine tests on-going.

4. **Collaboration:** ORNL, Umicore, and 3D Array Tech., and other labs (BNL, NETL) and universities (Georgia Tech, Arizona State U. and UT Dallas).
5. **Future work:**

a) More doping and loading studies on TiO_2/(Pt,Pd) systems for the 90% 150^{o}C THC conversion under CDC and LTC-D simulated exhaust conditions;
b) More mechanistic study on the water/S effects of TiO_2 based nano-array catalysts;
c) Large scale nano-array catalysts for engine dynamometer evaluation.

Any proposed future work is subject to change based on funding levels.

Acknowledgements

- Postdoc: Drs. Son Hoang, Wenxiang Tang, Andrew Binder, Eleni Kyriakidou

  Graduate students: Junfei Weng, Xingxu Lu, Sibo Wang, Wenqiao Song, Sheng-Yu Chen,

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- Collaborators: Drs. Zili Wu, Steven Overbury, Jim Parks (ORNL), Drs. Chang-Yong Nam (BNL), Dr. Yong Ding (Georgia Tech), Dr. Jingyue Liu (Arizona State U.), Dr. Jie Zheng (UT Dallas), Drs. John Baltrus, Paul Ohodnicki (NETL)
- Industrial partners: Corning, Umicore, 3D Array Tech..
- Project officers: Ken Howden, Ralph Nine
- DOE/NETL, NSF, DOE Office of Science User Facilities program (ORNL-CNMS, BNL-CFN)